

EFFICIENCY OF Cd, Zn AND Pb IMMOBILIZATION BY SOIL AMENDMENTS IMMEDIATELY AFTER THEIR APPLICATION

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ABSTRACT

The objective of this work was to evaluate the effectiveness of amendments in a contaminated soil to be restored using phytostabilization, immediately after the application of the additives. Metal concentration in pore-water was determined as metal bioavailability parameter. Fractionation on carbonate and exchangeable phases were also performed as an additional parameter to evaluate metal bioavailability in soil.

The studied soil originated from an abandoned open-cast mine in Toledo (Spain). Total Pb, Cd and Zn concentrations were higher than the threshold values of the Spanish legislation. Different additives were evaluated in a greenhouse experiment: two types of *cyclonic ash*, modified aluminosilicates originating from two different coal burning electricity plants using fluidised bed technology and *steel shots*, mainly consisting of iron oxides. Two weeks before sampling, pots were wetted at 50 % the water retention capacity with distilled water. Samples were taken after 15, 60, 100 and 205 days. Pore water extracts (Rhizon sampler) were analysed for determine Zn, Cd and Pb (ICP-AES). Soil samples were taken to evaluate pH, electrical conductivity total, exchangeable and carbonate adsorbed metals. At the end of the experiment, plants that spontaneously colonised the soil were harvested to assess Zn, Cd and Pb (ICP-AES) in the biomass.

Immediately after the application of the additives, metal concentration in pore water and exchangeable phase decreased was confirmed by Zn and Cd absorption by the plants. All these parameters seem to support that the presence of cyclonic ash improves the association of Zn and Cd to the less mobile phases. Although the Pb in the pore water solution decreased and the exchangeable fraction and the fraction specifically adsorbed to carbonates did not increase in soils treated with additives, the values found in plant questioned that this metal was immobilised in soils.

INTRODUCTION

Phytostabilization aims the *in situ* metal inactivation by means of revegetación either with or without non-toxic metal immobilizing or fertilizing soil amendments (Vangronsveld and Cunningham, 1998). Ideally, plants used in phytostabilization should be able to tolerate high levels of metals and immobilize them in soils by means of absorption, precipitation, complexation or change in the oxidation state. The effectiveness improves after the application of soil amendments, since these can modify the soil pH, nutritional conditions or microbial activities. Alternatively organic and inorganic amendments can be used. More than a real clean up of contaminated soil, the objective of phytostabilization is prevent in place the spread and transfer of trace elements, potentially toxic, to adjacent ecosystem and into the food chain (Vassilev *et al.*, 2004). Subsequently, vegetation can improve the physical stability of soil which reduces wind

erosion, surface runoff and water percolation (Vangronsveld *et al.*, 1996). Eventually a new ecosystem can develop (Vangronsveld *et al.*, 2000). Successful *in situ* immobilization can be achieved by changing the trace element speciation in the soil aiming to reduce the easily soluble and exchangeable fraction of these elements.

Industrial residues have been considered for their potential to immobilize toxic metals in polluted soils. Their use also results in a reduction of waste disposal through revalorization of industrial wastes into industrial co-products (Lombi *et al.*, 2002). Among others, cyclonic ash and steelshots have given good results in long term field experiments (Van der Lelie *et al.*, 2001). In Belgian industrial soils, near a zinc smelter, were treated with different amendments as compost, cyclonic ash and steelshots (Mench *et al.*, 1998). Results showed that metals (Cd, Zn and Pb) in the contaminated soils were mainly associated to the fractions that reduce their mobility (exchangeable and carbonate fractions). However, the combined use of organic and inorganic materials could diminish the metal proportion in the exchangeable phase that was redistributed to the reducible phase, reducing the mobility of the heavy metal. This process is not immediate, takes time and it is necessary to redistribute metals to the less mobility phases.

Phytostabilization is not an appropriate alternative for all metal contaminated sites. Factors such as pH, soil structure and metal combination need to be considered. The objective of this work is to evaluate if phytostabilization is suitable to inactivate heavy metals present in a degraded soil from Toledo (Spain), after the applications of amendments after a period of five months. Metal concentration in pore water solution (Knight *et al.*, 1997), as well as the association of this to the exchangeable phase and carbonates (Tessier *et al.*, 1979) are chosen as parameters of metal bioavailability.

METHODOLOGY

Soil characterization: The soil used came from an abandoned open-cast mine situated in Toledo (Spain). The soil characterization was made according to the Spanish Official Methods (1994): pH 7.3; Electrical Conductivity $180 \mu\text{S}\cdot\text{cm}^{-1}$; Organic Matter 3.19 %; total metal content was: Pb $7308 \text{ mg}\cdot\text{Kg}^{-1}$; Cd $30 \text{ mg}\cdot\text{Kg}^{-1}$; Cu, $81 \text{ mg}\cdot\text{Kg}^{-1}$; Ni $96 \text{ mg}\cdot\text{Kg}^{-1}$; Zn $5283 \text{ mg}\cdot\text{Kg}^{-1}$; Cr $48 \text{ mg}\cdot\text{Kg}^{-1}$. Pb ($>300 \text{ mg}\cdot\text{Kg}^{-1}$), Cd ($> 3.0 \text{ mg}\cdot\text{Kg}^{-1}$) and Zn ($> 450 \text{ mg}\cdot\text{Kg}^{-1}$) overcame threshold values of the European legislation (Directive 86/278/CEE).

Choice of amendments: Two industrial by-products were used as amendments: cyclonic ash and steel shot. Amendments selection and suitable doses were chosen according to Mench *et al.*, (1998). The cyclonic ashes (CAR and BAH) originated from two different fluidised bed coal powered electricity plants. Steelshot (SS) contain mainly iron oxides (97%) and impurities such as Mn (0.6 -1 %), Si (0.8 to 1.2 %) and Cr (0.2-0.5%).

Greenhouse experiment: A pot experiment was carried out in a research greenhouse at The University of Limburg, (Diepenbeek, Belgium) during six months. Soil was air dried, sieved ($<2 \text{ mm}$) and amended using the following treatments: (S) untreated soil; (SSS) soil + 1% steelshots; (SCAR) soil +5% cyclonic ash CAR; (SSSCAR) soil +1% steelshots + 5% cyclonic ash CAR; (SBAH) Soil +5 % cyclonic ash BAH; (SSSBAH) soil +1% steelshots +5% cyclonic ash BAH. Amended soils were putted in plastic pots with 12,5 cm diameter and containing 1 Kg of soil. Three replicates of each treatment were made.

Pore water sampling: In order to evaluate metal mobility, Rhizon soil moisture samplers were used to extract soil pore water. The method had been detailed by Knight

et al. (1997) and Chaudri *et al.* (1999). Before using, all the samplers were washed with 60 mL of 5% HNO_3 , 60 mL of deionised water and then dried at room temperature. One sampler was placed diagonally from the lip of the pot to the base into each replicate. The soil was brought to 50% water holding capacity and maintained by addition of deionised water. Two weeks prior to the extraction, the soils were brought to 75% of water holding capacity (time 0). Samples were also taken at 15, 60, 100 and 205 days. An aliquot from the extracted soil solution was acidified with 0.3% HNO_3 and Zn, Cd and Pb were determined by ICP-AES.

Soil analysis Soil samples were taken for chemical analysis from each of the treatments (0, 60, 100 days). Samples were air-dried and ground in an agate mortar before analysis. Electrical conductivity and pH were measured in a water extract (1:2.5). Total Cd, Pb and Zn concentrations were measured by ICP-AES after microwave digestion in HNO_3 :HCl. Exchangeable metal concentration and metals specifically adsorbed to the soil carbonates were determined according to Hudson-Edwards *et al.*, (1998) from modified methods of Chao, (1972) and Tessier *et al.*, (1979). As reagent for the selective extraction of exchangeable metals MgCl_2 (1 M pH 7, 1:10 w/v, 1 h) was used. The fraction of metal specifically adsorbed to carbonates is obtained from the resulting precipitate from exchangeable phase by addition CH_3COONa 1M at pH 5 (CH_3COOH , 1:10 w/v 5 h). All metal concentrations were measured in the extracts by ICP-AES.

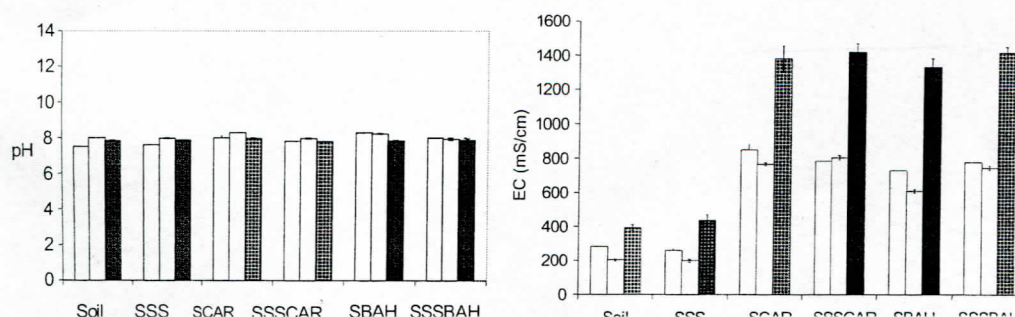
Plant analysis Spontaneous colonisation by plants took place on the experimental pots. All the plants were harvest after 3 months of growth, washed with distilled water and weighed. Afterwards, they were dried in a forced air oven at 60 C during three days. Then, dry weight was determined and plant material was grounded in an agate mortar. The total metal content was analysed after microwave digestion with HCl : HNO_3 by ICP-AES.

Statistical analysis. Analysis of variance was performed using SAS version 5 (1985). The data, except all of the soil analysis corresponding to time 0, were subjected to ANOVA. Differences between means were determined using Duncan test.

RESULTS AND DISCUSSION

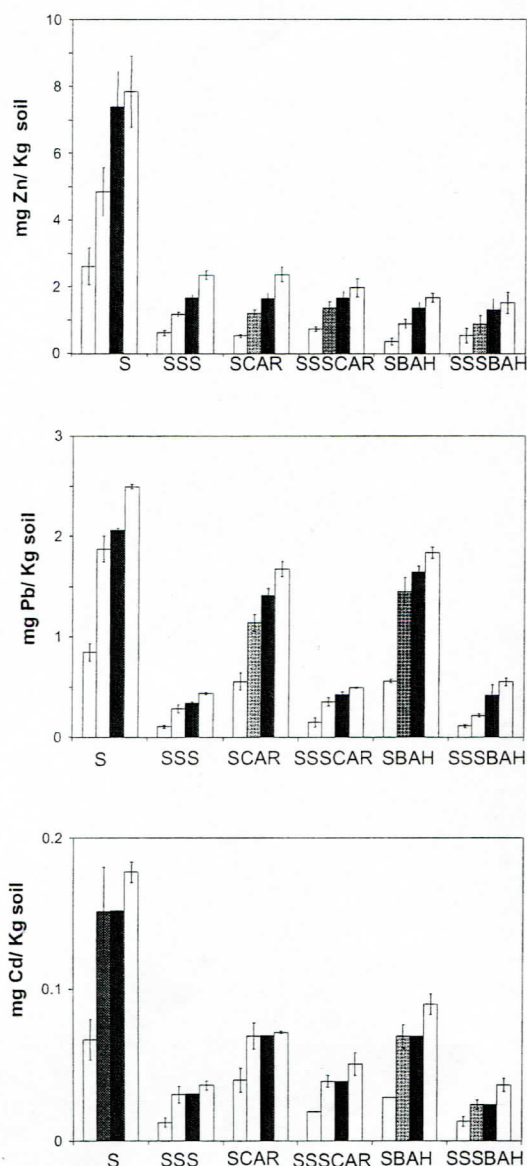
Soil analysis According to Mench *et al.* (1998), the addition of cyclonic ash to soil promotes the sorption process. Initially a rapid first step representing adsorption onto highly accessible sites on surface on binding sites of original soil components freed due to a liming effect, followed by slower type of sorption characteristic for modified surfaces and, finally, the longer term crystal growth. Moreover, the amount of trace elements adsorbed on a solid phase depended, among other factors, on the nature of additives and soil pH.

Figure 1 pH and Electrical conductivity of soil and amended soils to be used in phytostabilization. Days 0 open columns; dotted columns 60 days; hatched columns, 100 days. Error bars indicated SEs. (n=3).



Previous studies performed on acid soils reported significant increments in pH soils

Figure 2 Total Zn, Cd and Pb concentrations in pore water in the different treatments. Days 0: open columns; hatched columns, 65 days; black columns, 100 days; dotted columns 205 days. Error bars indicated SEs.



amended with cyclonic ash and steel shots for 100 days (Geebelen *et al.*, 2002; Mench *et al.*, 1994ab; Vangronsveld *et al.*, 1995a,b). The soil studied here had an initial pH value of 7.3, which is considered as high. Therefore, an increase of this parameter is not desired in order to avoid micronutrients deficiency in plants. The influence of the additives on pH is presented in figure 1. After 60 days both types of cyclonic ash significantly increased the pH value, probably due to the liming effect describe above, however, this effect did not last long time, and the pH stabilized around 7.8.

Data of electrical conductivity in the pots are also given in figure 1. In general, treatments that included cyclonic ash and their combinations with steel shots significantly increased EC values. This effect was also described by other authors (Geeleben *et al.*, (2002); Mench *et al.*, 1998). They reported that consequence of cyclonic ash application was the excessive soluble salt concentration in soils, which might generate increased concentrations of potentially toxic trace elements, and also, adverse effects on soil properties (e.g., cementation).

Pore water concentrations of Zn, Pb and Cd in the untreated soil significantly increased during the period of investigation (205 days). Availability of metals should decrease after application of cyclonic ash. Figure 2 shows that addition of soil amendments indeed resulted in significant decreases of Zn, Cd and Pb concentrations in pore water. The differences are strongest at the beginning of treatments, when the metals found new adsorption sites.

The lowest metal concentrations were found in the pore water of soils treated with steel shots, alone or steel shots combined with cyclonic ash. Cyclonic ash alone clearly was not very

efficient to immobilise Pb and Cd. In all cases, untreated soils showed the highest metal contents in pore water solution.

Table 1 Percentage (%) of exchangeable and specifically adsorbed metals from the total metal in different treatments

	Days	Exchangeable (%)			Adsorbed (%)		
		Zn	Pb	Cd	Zn	Pb	Cd
Soil	0	1.15	0.50	20	20	17	20
	60	0.72 a	0.24 a	23 ab	17 a	15 ab	22 ab
	100	0.43 a	0.28 a	11 a	12	8 bc	16
SSS	0	1.04	0.35	28	16	14	22
	60	0.76 a	0.24 a	35 a	16 a	16 a	22 b
	100	0.31 b	0.12 bc	11 a	13	10 ab	18
SCAR	0	0.03	0.22	29	17	18	26
	60	0.16 b	0.16 b	10 b	16 a	19 a	27 a
	100	0.08 b	0.14 b	9 ab	10	11 a	19
SSSCAR	0	0.16	0.11	16	15	18	27
	60	0.22 b	0.14 b	11 b	12 b	9 b	24 ab
	100	0.11 c	0.08 b	7 b	11	8 bc	18
SBAH	0	0.26	0.20	43	20	19	32
	60	0.19 b	0.15 b	10 b	16 a	11 ab	24 ab
	100	0.12 c	0.14 b	8 ab	10	6.5 c	17
SSSBAH	0	0.32	0.14	30	17	13	34
	60	0.24 b	0.14 b	10 b	13 b	10 ab	20 b
	100	0.14 c	0.13 b	8 ab	10	9 bc	17
M		***	*	***	***	**	***
T		***	**	***	**	**	N.S.
M*T		**	***	**	N.S.	N.S.	N.S.

Different letters means significant differences among treatments at the same sampling time
 ***, $p < 0.001$. **, $p < 0.01$, *, $P < 0.05$; NS, not significant.

Tessier *et al.*, (1979) operationally defined the exchangeable metal as loosely bound cations and anions, and specifically adsorbed metal as bound to carbonates and the most reactive oxyhydroxides. In comparison to the untreated soil, application of cyclonic ash decreased the percentage of metals in the exchangeable fraction. Differences are statically significant for both types of cyclonic ash applied alone or combined with steel shots, also, for the three studied metals. The effect increased along the experiment. The nature of the cyclonic ash does not seem to affect the concentration of exchangeable Zn and Cd. The effect of steel shots seems to

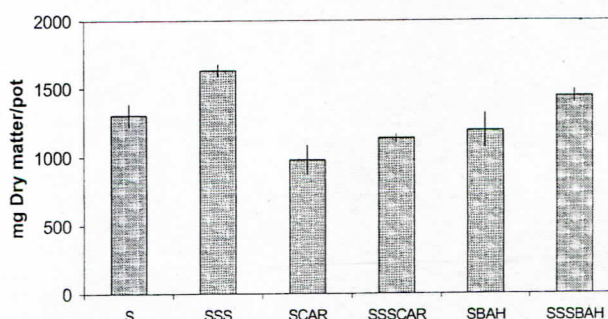


Figure 3 Spontaneous biomass production in each of the treatments after 100 days application (mg dry mass·pot⁻¹). Error bars means SEs (n=3).

be slower. Initially no significant differences were observed with the untreated control; after 200 days, significant reductions were observed for exchangeable Zn and Pb. In case of Pb, the concentration of this metal in the exchangeable phase is affected by the nature of the ash and improved in presence of the steelshots especially after longer periods (Table 1). The most effective treatment was BAH ash combined with steel shots (SSSBAH). Such a global result was not observed for metals associated to the carbonate phase. No significant differences were found for t Cd coming from the treatments control and the rest of the treatments. In case of Zn, a slight effect is observed at two months after the start of the experiment, showing the lowest values after treatment with cyclonic ash combined with steel shots. However, this effect disappeared after 200 days of treatment, at that moment similar values were reached in all cases.

Plant analysis The higher production of biomass (figure 3) was registered in the pots treated exclusively with steel shots and steels shoots combined with BAH ash. On the contrary, addition of the other cyclonic ash CAR and its combination with the steel shots resulted in the lowest biomass production. In the case of untreated soils, intermediate values were found.

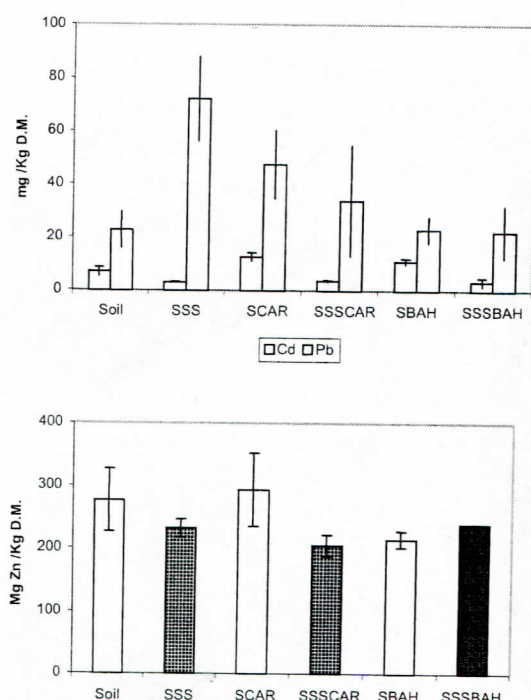


Figure 4 Total Cd, Pb and Zn ($\text{mg} \cdot \text{Kg}^{-1}$ DM) in plants grown on amended soils. Error bars SEs ($n=3$).

Gramineous species were dominating the spontaneous colonisation of the pots. Total foliar contents of Pb, Zn and Cd were determined. Concerning the mobility of metals in the soils as illustrated by metal content in pore water solution, exchangeable and metals adsorbed to the carbonates, plants growth on untreated soil showed the lowest values for Pb (figure 4). The plants treated with cyclonic ash, alone or in combination with steel shots showed the lowest values in Cd. However, when the cyclonic ashes were applied alone, the levels of Cd in plants were significantly higher than the untreated.

On the other hand, for Pb, the highest values were found in the plants cultivated on soils treated with steel shots; these values were significantly higher in comparison to the other treatments. No big effects of additive treatment were found for Zn content in aerial parts of the plants.

Steelshots and the combinations with cyclonic ash seem promising for Cd immobilization. All the parameters studied here showed that Cd was associated to phases that are less mobile. The highest values found for electrical conductivity in soils treated with cyclonic ash and its combinations need

to be carefully evaluated in order to use this additives. However, the low levels Pb, Zn and Cd found in the exchangeable and specifically adsorbed fractions suggest that the

metals do not occur as soluble ions or flocculation of colloids in soils treated with cyclonic ash.

CONCLUSIONS

The application of additives such as cyclonic ash and steel shots has been studied for use in metal phytostabilization. In an experiment performed under controlled conditions, results have shown that:

- The pH of the contaminated soil increased immediately after the cyclonic ash application. No effect was found after addition of steel shots and the combination of additives.
- Electrical conductivity was seriously increased after cyclonic ash applications.
- The application of steel shots generated the highest biomass production
- Addition of the soil additives led to decreases of metal concentration in the pore water and the exchangeable fraction. For Zn and Cd this was confirmed by the metal contents measured in the plants colonizing the soils. This suggests that the presence of cyclonic ash increases the association of Zn and Cd to less mobile phases. On the contrary lead concentration in the pore water also decreased, but the contents found in plants questioned that this metal should be immobilized.

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